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UCID- 18509-80-1

**DEVELOPMENT OF ADVANCED TECHNOLOGIES
FOR PHOTOCHEMICAL TRITIUM RECOVERY**

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A Quarterly Program Report for the period
January 1, 1980 through March 31, 1980, prepared
for the use of the staff of the Nuclear
Materials Production Office of the U. S.
Department of Energy.

April 23, 1980



Lawrence
Livermore
Laboratory

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Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.

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DEVELOPMENT OF ADVANCED TECHNOLOGIES
FOR PHOTOCHEMICAL TRITIUM RECOVERY

Quarterly Progress Report
For the Period January 1, 1980 Through March 31, 1980

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ABSTRACT

Progress has been made in building the laboratory facility for photochemical tritium separation research. Initial IR photolysis experiments have been performed in $\text{CDCl}_3/\text{CHCl}_3$ to better understand the photochemistry in the $\text{CTCl}_3/\text{CDCl}_3$ system anticipated to be useful in photochemical tritium recovery.

During this quarter active preparation of laboratory facilities for tritium recovery experimentation began in the Lawrence Livermore Laboratory Tritium Building. These facilities should be nearing completion in the coming quarter. The photochemical properties of some working molecules of interest in T/D separation began this quarter by analysis of the properties of the non-tritiated molecules.

Optical Selectivity

Based on the calculated spectra of several monotrinitated halogenated methanes presented in the previous quarterly report¹, trichloromethane emerged as an attractive candidate for tritium recovery from heavy water. In addition, dichloromethane appeared to be interesting since preliminary calculations¹ have shown it to have T/D selective bands near 924 and 938 cm^{-1} . To estimate potential optical selectivity in absorption, one infrared spectra of CDCl_3 and CD_2Cl_3 have now been measured at higher pressures near the spectral regions of interest. These are shown in Figures 1 and 2, which also indicate the anticipated location of the tritium-selective absorption regions. If one assumes that the tritiated molecule has absorption band strengths comparable to the deuterated molecule, then the optical selectivities may be estimated as in Table I, based on linear absorption strengths.

Photochemistry of Trichloromethane

The photochemistry of trichloromethane was investigated, since it has emerged as an attractive candidate molecule.¹ In order to study trichloromethane, CDCl_3 was photolysed at 914 cm^{-1} using the P(50) line of a LUMONICS 103 TEA CO_2 Laser. Since the photodissociation pathways for the different isotopes should be the same, analysis of CDCl_3 is expected to illuminate both the primary decomposition step and the succeeding chemistry for CTCl_3 also. The output

energy of the laser at this wavelength was 1.5-2 joules/pulse, and when focussed into a 60 cm length all using a 100 cm focal length lens, it resulted in a peak focal fluence of 12-18 joules/cm². The primary observed photoproducts were DCl, which was present, but not detected by GC using flame ionization, 1,1-dichloroethylene, trichloroethylene, tetrachloroethylene and tetrachloromethane. These products are different from the results of chloroform pyrolysis² where 1,1-dichloroethylene was not detected, but is the major laser produced photoproduct. Yields for photolysis of neat CCl₃ at 0.1-0.5 torr were measured by gas chromatograph using flame ionization. Yields are approximately as given in Table II.

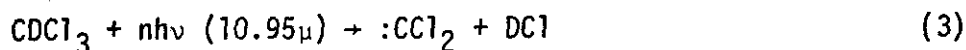
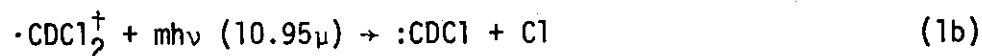
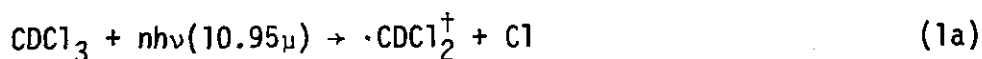
Table II

Trichloromethane Photoproduct Yields

<u>Photoproduct</u>	<u>Normalized Yield*/Pulse</u>
1,1-dichloroethylene	0.42
Tetrachloromethane	0.09
Trichloroethylene	0.03
Tetrachloroethylene	0.38
Dichloromethane	0.00

*Fraction of CCl₃ molecules within the focal region that decompose per pulse to yield the indicated photoproduct molecule.

The following steps can explain the observed photoproducts:



Trichloromethane absorbs infrared light and eliminates a Cl atom in step (1a), producing a vibrationally excited $\cdot\text{CDCl}_2^+$ radical, which continues to absorb light yielding a $:\text{CDCl}$ radical and a second Cl atom in step (1b). The $:\text{CDCl}$ radicals recombine in step (2) to yield the primary observed 1,1-dichloroethylene photoproduct. Molecular elimination of DCl in step (3) can also occur yielding $:\text{CCl}_2$ radicals that recombine to form the second main photoproduct, tetrachloroethylene, in step (3). The Cl atoms formed in step (1) can attack trichloromethane to abstract hydrogen to form hydrogen chloride in step (5), followed by formation of CCl_4 in step (6). The $:\text{CDCl}$ and $:\text{CCl}$ radicals formed in steps (1) and (3) could also recombine to form trichloroethylene in step (7).

The two primary dissociation channels are atomic elimination, step (1), and molecular elimination, step (3). In an effort to try to determine this dissociation branching ratio HI was added as a scavenger. HI will donate hydrogen to radicals according to the steps:



Dichloromethane can result from atomic elimination through step (8). It may also be formed from molecular elimination via steps (11), (12) and (8) only if CCl_2HI formed in step (11) is energetically unstable. Step (12) appears to be slightly exoergic and at present it appears that dichloromethane may be formed via the molecular route also. Some methyl chloride could form via steps (9)-(10). Negligable amounts of methyl chloride were observed, however, when HI was added.

Instead, much dichloromethylene was observed, and the dichloromethane yields increased with added HI, as shown in Table III.

Table III

The Effect of Added HI on Dichloromethane Yields in CDCl_3 Photolysis

<u>Initial Composition</u>	<u>Dichloromethane/1,1-Dichloroethylene Photoproduct Ratio</u>
0.32 torr CDCl_3	0.0
0.32 t CDCl_3 + 0.16 t HI	2.2
0.32 t CDCl_3 + 0.32 t HI	3.1
0.32 t CDCl_3 + 0.74 t HI	5.6

Though presently this technique does not appear to distinguish between atomic and molecular elimination, since both channels can ultimately yield dichloromethane, the atomic elimination channel is expected to dominate at higher fluences. The effect of both fluence and added argon buffer gas on photoproduct yield will be evaluated during the coming reporting period.

Isotopic Scrambling

In an actual process using trichloromethane, chlorine atom reactions (5) and (6) could result in scrambling according to the process:



To test this a equimolar mixture of CDCl_3 and CHCl_3 , the D/H analog, was prepared and irradiated at 914 cm^{-1} at $153/\text{cm}^2$ fluence for 650 pulses. IR spectroscopy showed a two-fold decrease in the CDCl_3 bands, with no detectable decrease in CHCl_3 . Thus, radical reactions according to equation (15) or (16) must not be important under these conditions, since otherwise a significant decrease in the CHCl_3 would have ensued. This is a good omen for successful T/D separation.

References

1. I. P. Herman and J. B. Marling, "Development of Advanced Technologies for Photochemical Tritium Recovery", University of California Lawrence Livermore Laboratory Report No. UCID-18509-79-4, January, 1980.
2. G. LeMoan, "Pyrolytic Decomposition of Chlorinated Methane Derivatives in the Absence of Oxygen and up to 720°", Comptes Rendue, 260, 55 88 (1965).

Table I

Anticipated Optical Selectivity for Prospective Tritiated Working Molecules

<u>System</u>	<u>Frequency</u>	<u>Absorption Coefficient for Totally Deuterated Molecule</u>	<u>Expected Linear Selectivity</u>	<u>at Frequency</u>
CTCl ₃ /CDCl ₃	914 cm ⁻¹ *	5.7 x 10 ⁻² torr ⁻¹ cm ⁻¹ *	>3000	830cm ⁻¹ **
CTCl ₃ /CDCl ₃	830 cm ⁻¹	<1.4 x 10 ⁻⁵ torr ⁻¹ cm ⁻¹		
CDTC1 ₂ /CD ₂ Cl ₂	952 cm ⁻¹ *	1.2 x 10 ⁻² torr ⁻¹ cm ⁻¹ *	1000-2000	912cm ⁻¹ ***
CDTC1 ₂ /CD ₂ Cl ₂	912 cm ⁻¹	~0.9 x 10 ⁻⁵ torr ⁻¹ cm ⁻¹		

* Transition Frequency and Absorption Coefficient of a totally deuterated molecule which is an analog of the monotrinitated feature of interest (listed in the next line in the table).

** Calculated frequency of ν_5 mode of CTCl₃.

*** On the red, P-branch side on expected 920-940cm⁻¹ CDTCL₂ transitions.